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## Evolution of cation and spin orders in the double – double double perovskite series

### $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$

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## Abstract

Variations of perovskite superstructure type and magnetic properties across the high pressure  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  series have been investigated by powder neutron diffraction, x-ray magnetic circular dichroism, and magnetisation measurements. Monoclinic  $P2_1/n$   $A_2BB'\text{O}_6$  double perovskite solid solutions with rocksalt type ordering of  $B/B'$ -Fe/Re cations but no  $A$ -cation order are discovered to exist only close to the end members  $0 < x < 0.17$  and  $1.73 < x < 2$ . Compositions in the range  $0.74 < x < 1.1$  adopt a tetragonal  $P4_2/n$   $AA'BB'\text{O}_6$  double double perovskite phase based on  $\text{CaMnFeReO}_6$ , which has both columnar  $A/A'$ -Ca/Mn and rocksalt  $B/B'$ -Fe/Re cation orders. Two-phase coexistence of double and double double perovskites occurs over wide regions between these limits. All samples are ferrimagnetic with Curie temperatures near 500 K. Low temperature Mn spin order is also observed in the Mn-rich double perovskites and the double double perovskites. Spin reorientation transitions observed across all of the double perovskites are shown to result from  $5d^2$   $\text{Re}^{5+}$  orbital ordering, but this does not occur in the double double perovskites. The Ca-rich double perovskites show significant magnetic coercivity at low temperatures.

## Introduction

$ABO_3$  perovskite oxide materials have many outstanding physical properties and these can be further tuned through structural variations arising from cation order. Cation order of two different  $A$  or  $B$ -site cations in a 1:1 ratio leads to structural derivatives known as double perovskites [1]. These types of 1:1 order can occur with rock salt, columnar and layered arrangements. The most common form of double perovskites possesses a 1:1 rock salt order of  $B/B'$  cations, with a general formula of  $A_2BB'O_6$ , often with a large charge difference between  $B$  and  $B'$  that promotes cation order through minimising electrostatic repulsion [2]. Less commonly, some perovskites display long range orders of different cations of both the  $A$  and the  $B$ -site cations [1] and these  $AA'BB'O_6$  materials are described here as ‘double double perovskites’, for example,  $\text{CaMnFeReO}_6$  as shown in Fig. 1 and described further below.

$A_2BB'O_6$  double perovskites with a 1:1 rock salt order of  $B/B'$  cations may exhibit ferrimagnetic and half metallic behaviours in cases where large spin  $3d$   $B$  cations and small spin  $4d$  or  $5d$   $B'$  cations are well ordered, as in the well-known example of  $\text{Sr}_2\text{FeMoO}_6$  [3,4], and related materials [5] such as  $\text{Ca}_2\text{FeReO}_6$  [6]. However, the latter is more complex [7,8,9,10,11] as it undergoes a phase transition from a ferrimagnetic metallic to a ferrimagnetic insulating phase below 140 K, which has been identified as the orbital ordering transition for the  $5d^2$  state of  $\text{Re}^{5+}$  [12], and other phenomena such as electronic phase separation based on different spin-orbit coupled orders are also reported [13,14]. These  $A_2BB'O_6$  double perovskites stabilized by non-magnetic  $A$ -site cations such as  $A = \text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$  are typically prepared at ambient pressure, but it has recently been shown that analogs with the magnetic transition metal cation  $\text{Mn}^{2+}$  ( $3d^5$ , spin  $S = 5/2$ ) at the  $A$ -site can be prepared at high temperatures, for example,  $\text{Mn}_2\text{BSbO}_6$  ( $B = \text{Sc}$  [15],  $\text{Cr}$  [16], and  $\text{Fe}$  [17]),  $\text{Mn}_2\text{BReO}_6$  ( $B = \text{Mn}$  [18,19],  $\text{Fe}$  [20,21] and  $\text{Co}$  [22]),  $\text{Mn}_2(\text{Fe}_{0.8}\text{Mo}_{0.2})\text{MoO}_6$  [23] and  $\text{Mn}_2\text{MnTeO}_6$  [24].  $\text{Mn}_2\text{FeReO}_6$  is notable as having a ferrimagnetic insulating ground state similar to that of  $\text{Ca}_2\text{FeReO}_6$ , a high Curie temperature of  $T_C = 520$  K, a large magnetisation of  $5.0 \mu_B/\text{f.u.}^{-1}$  at 75 K (f.u. = formula unit), and low temperature switching of the sign of magnetoresistance attributed to magnetic frustration between  $A$ -site  $\text{Mn}$  and  $B/B'$ -site  $\text{Fe/Re}$  spins. When half of the  $\text{Mn}^{2+}$  was replaced by  $\text{Ca}^{2+}$ , the product  $\text{CaMnFeReO}_6$  was found to have an  $AA'BB'O_6$  double double perovskite structure with columnar 1:1  $A/A'$ -site order of 10-coordinate  $\text{Ca}^{2+}$  and 4-coordinate  $\text{Mn}^{2+}$  as well as rocksalt 1:1  $B/B'$ - $\text{Fe/Re}$  cation order [25]. This tetragonal  $P4_2/n$  double double perovskite structure type is also observed in the  $\text{RMnMnSbO}_6$  ( $R = \text{La}$ ,  $\text{Pr}$ ,  $\text{Nd}$ ,  $\text{Sm}$  [26,27]) series as well as in  $\text{CaMnMReO}_6$  ( $M = \text{Mn}$  [25],  $\text{Co}$  and  $\text{Ni}$  [28]) and  $\text{Ca}(\text{Mn}_{0.5}\text{Cu}_{0.5})\text{FeReO}_6$  [25]. These double double perovskites all require high pressure synthesis.

$\text{Mn}_2\text{FeReO}_6$  and  $\text{Ca}_2\text{FeReO}_6$  both have monoclinic  $P2_1/n$  double perovskite structures, so the above observation that their apparent  $x = 1$  solid solution  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  in fact has a higher symmetry tetragonal  $P4_2/n$  double double perovskite structure is unusual and has motivated the present study. Similar structural changes were not reported in other mixed-cation double perovskite systems [5]. Here,

two further samples with nominal compositions  $x = 0.5$  and  $1.5$  have been prepared at high pressures to discover how structural properties and cation orders evolve between the double perovskites at  $x = 0$  and  $2$ , and the double double type at  $x = 1$ . Investigations of magnetic properties and crystal and magnetic structures for the previously reported  $x = 0$  and  $1$  and the new  $x = 0.5$  and  $1.5$  samples are used to explore how phase formation and structure type, high-temperature ferrimagnetic order of Fe/Re spins, and low temperature  $\text{Mn}^{2+}$  spin-ordering,  $\text{Re}^{6+}$  orbital-ordering, and spin-reorientation transitions previously reported in the  $x = 0$  and  $2$  end-members, vary with doping. Results for samples with nominal  $x = 0, 0.5, 1.0$  and  $1.5$  compositions will be presented, followed by a discussion of the structural, and magnetic properties across the proposed  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  phase diagram.

## Experimental

Polycrystalline  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  samples were prepared by high pressure synthesis at 10 GPa and 1673 K in a Walker-type multianvil module. The starting materials which were mixed in stoichiometric proportions were:  $x = 0$  –  $\text{Mn}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{ReO}_2$ ;  $x = 0.5$  –  $\text{CaMnO}_3$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{ReO}_2$ ;  $x = 1$  –  $\text{CaMnO}_3$ ,  $\text{Ca}_2\text{Fe}_2\text{O}_5$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{ReO}_2$ ; and  $x = 1.5$  –  $\text{CaMnO}_3$ ,  $\text{Ca}_2\text{Fe}_2\text{O}_5$  and  $\text{ReO}_2$ .

Powder Neutron Diffraction (PND) was performed on ~60 mg of each of these samples using the WISH diffractometer at the ISIS Neutron Facility [29], at temperatures from 2 to 300 K. Powder synchrotron X-ray diffraction (PSXRD) data were collected for  $\text{CaMnFeReO}_6$  at the BL04-MSPD beamline at the ALBA facility (wavelength  $\lambda = 0.44214$  Å). Room temperature PSXRD was also performed on the  $x = 0.5$  and  $1.5$  samples on beamline ID22 at the ESRF ( $\lambda = 0.39987$  Å). The FullProf Suite was used to analyse the powder diffraction data [30]. The neutron scattering lengths for Ca, Mn, Fe, and Re of 4.70, -3.73, 9.45 and 9.2 fm, respectively, gave high contrast between the lighter metals Ca, Mn, and Fe in PND site occupancy refinements from which Ca/Mn ratios in the components of multi-phase samples were determined. X-ray refinements were used to quantify any B/B'-Fe/Re antisite disorder.

X-ray Absorption Near-Edge Spectra (XANES) used to derive X-ray Magnetic Circular Dichroism (XMCD) data were collected at the Re  $L_2$ , Re  $L_3$  and Mn K edges on beamline ID12 at the ESRF, at temperatures from 2 to 300 K and in applied field strengths up to 17 T. The fluorescence of the samples was measured in backscattering geometry and the X-ray absorption spectra were corrected for self-absorption effects.

The zero-field cooled and field-cooled thermal dependence of magnetisation (under an applied field of 0.5 T) was measured for all materials between 5 and 650 K and magnetic hysteresis loops were recorded in fields up to 7 T.

## Results

### 1. Powder Diffraction

#### **Mn<sub>2</sub>FeReO<sub>6</sub> ( $x = 0$ )**

Mn<sub>2</sub>FeReO<sub>6</sub> is notable as the first reported example of a double perovskite with all cation sites occupied by magnetic transition metal ions [20,21]; *A*-site Mn<sup>2+</sup> ( $3d^5$ ,  $S = 5/2$ ) and *B*-site Fe<sup>3+</sup> ( $3d^5$ ,  $S = 5/2$ ) and Re<sup>5+</sup> ( $5d^2$ ,  $S = 1$ ). Ferrimagnetic Fe and Re spin ordering occurs at  $T_C = 520$  K and an additional antiferromagnetic order of *A*-site Mn<sup>2+</sup> spins was observed below  $T_{Mn} = 150$  K leading to a spin reorientation transition of all sublattices due to frustration at  $T_{sr} = 75$  K. The material reaches a maximum magnetisation of  $5.0 \mu_B \cdot \text{f.u.}^{-1}$  (the largest reported value for transition metal based double perovskites) at 75 K and falls on further cooling. The sign of magnetoresistance switches from negative above the canting transition ( $MR = -19\%$  at 7 T, 100 K) to positive below ( $MR = +265\%$  at 7 T, 20 K).

New high-resolution PND data obtained on this material using the WISH Diffractometer have enabled a more thorough refinement of the magnetic structures and associated structural distortions to be carried out. The structural symmetry is monoclinic  $P2_1/n$  throughout and the spin structures have propagation vector  $\mathbf{k} = (0 \ 0 \ 0)$  with Irreducible Representations as shown previously [21]. No *A/B* antisite disorder was found in initial fits to PND data, and all sites were fixed at full occupancy. Room temperature lattice parameters and magnetic transition temperatures for Mn<sub>2</sub>FeReO<sub>6</sub> and other Ca<sub>x</sub>Mn<sub>2-x</sub>FeReO<sub>6</sub> samples are shown in Table I. Full tables of refined structural and magnetic parameters for Mn<sub>2</sub>FeReO<sub>6</sub> are shown in [31] and results are summarised in Figs. 2 and 3. Magnetic diffraction from only ferrimagnetic order of Fe/Re spins is present at 200 – 300 K. This was previously fitted with moments parallel to the *c*-axis [21], but the present study showed that these spins lie in the *ac*-plane with both components active, e.g.  $m_x = 1.7(2)$  and  $m_z = 3.68(8) \mu_B$  at 200 K [31]. Re moments are too small to be refined independently and so Re spin components were constrained to have -20% of Fe spin values, as used previously [21]. Induced antiferromagnetic order of *A*-site Mn spins is observed to emerge between 175 and 200 K, and refinements give three Cartesian spin components of comparable magnitude, e.g.  $m_x = 1.20(7)$ ,  $m_y = 0.98(8)$  and  $m_z = 1.35(6) \mu_B$  at 80 K. Both Fe/Re and Mn spins were fitted with three Cartesian spin components below the 75 K canting transition. Magnetostructural coupling is apparent as anomalies in the thermal evolution of lattice parameters and some Fe-O and Re-O bonds are observed at the spin canting transition at 75 K (Fig. 2). The expansion of one of the pairs of Re-O bond distances below  $T_{sr} = 75$  K is similar to that reported for the Re<sup>5+</sup> orbital ordering transition in Ca<sub>2</sub>FeReO<sub>6</sub> at 140 K which also drives a spin reorientation [12]. This suggests that a coupled Re<sup>5+</sup> orbital ordering and spin reorientation transition occurs in both Mn<sub>2</sub>FeReO<sub>6</sub> and Ca<sub>2</sub>FeReO<sub>6</sub> at low temperatures (and this is supported by observations on intermediate double perovskite phases in the following sections).

The ordered spin structures at representative temperatures are shown in Fig. 3a. Thermal variations of spin components and tilt angles in Fig 3b show that the ferrimagnetic Fe/Re spins are tilted by  $\sim 25^\circ$  from the  $c$ -direction in the  $ac$ -plane at high temperatures, which corresponds to the  $\theta_{\text{Tilt}}$  tilting angle of the  $\text{FeO}_6$  octahedra so this likely defines the easy-axis. Antiferromagnetic Mn order emerges below 200 K and the canting transition at 75 K tilts Fe/Re moments further to  $50^\circ$  from  $c$ , and adds a small antiferromagnetic component of  $0.5 \mu_B$  for Fe parallel to the  $b$ -axis. The introduced tilting angle for the Fe moment in the  $ab$ -plane  $\phi_{\text{Fe}} \approx 12^\circ$  is close to the corresponding octahedral tilt angle  $\phi_{\text{Tilt}}$ , showing that local structure again determines the easy-axis. The Fe moments are essentially fully ordered, with a magnitude of  $4.9 \mu_B$  at 1.5 K, and are canted by  $24^\circ$  from the directions of their neighbors in successive  $ac$ -layers, which gives rise to the positive magnetoresistance effect described previously [21].

### **$\text{Ca}_{0.5}\text{Mn}_{1.5}\text{FeReO}_6$ ( $x = 0.5$ )**

This composition has the ideal cation ratio to form a 1:3  $A$ -site and 1:1  $B$ -site ordered perovskite, as observed in  $\text{CaCu}_3\text{Fe}_2\text{Re}_2\text{O}_{12}$  [32]. However, this ordering type was not observed and samples prepared with the nominal  $x = 0.5$  composition were found to consist of two phases. One is a double perovskite with monoclinic  $P2_1/n$  symmetry, like  $\text{Mn}_2\text{FeReO}_6$  above, and the other is a double double perovskite with tetragonal  $P4_2/n$  symmetry having 1:1 orders of  $A$  and  $B$  site cations as found in  $\text{CaMnFeReO}_6$  [25]. These phases are labelled as  $x = 0.5(\text{M})$  and  $x = 0.5(\text{T})$  respectively. The structures of both materials were fitted to PSXRD and PND data as shown in Fig. 4. Full tables of refined structural and magnetic parameters are shown in [31]. The two phases are found to coexist in approximately equal proportions, with refined weight fractions of 49(3)% of 0.5(M) and 51% of 0.5(T) from PND fits.

To explore whether the chemical compositions of the  $x = 0.5(\text{M})$  and  $x = 0.5(\text{T})$  phases differ from the nominal value,  $A$ -site Ca/Mn ratios were refined in fits to the PND data. The  $x = 0.5(\text{M})$  phase has a nominal  $(\text{Ca}_{0.5}\text{Mn}_{1.5})\text{FeReO}_6$  double perovskite formulation, but the refined composition was  $(\text{Ca}_{0.17(3)}\text{Mn}_{1.83})\text{FeReO}_6$  showing that it is Ca-poor relative to the average composition. The  $x = 0.5(\text{T})$  phase would have nominal composition  $(\text{Ca}_{0.5}\text{Mn}_{0.5})\text{MnFeReO}_6$  as a double double perovskite, but refinement gave  $(\text{Ca}_{0.74(2)}\text{Mn}_{0.26})\text{MnFeReO}_6$  demonstrating that it is Ca-rich. The observation that the  $x = 0.5(\text{M})$  and  $x = 0.5(\text{T})$  phases have respective refined  $x$  values of 0.17(3) and 0.74(2) clearly demonstrates that a chemical phase separation (miscibility gap) exists in this region of the  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  system under the given synthesis conditions. A Ca-poor double perovskite phase exists over the approximate range  $0 < x < 0.17$ , a double double perovskite is found for  $x > 0.74$ , and two-phase coexistence occurs between these limits. Similar amounts of  $B/B'$ -Fe/Re antisite disorder were found in the two structures from PSXRD refinements [5.8(1)% for  $x = 0.5(\text{M})$  and 5.0(1)% for  $x = 0.5(\text{T})$ ] demonstrating that the  $B/B'$  site ordering is unaffected by the phase separation and differences between the double and double double perovskite structures.

The  $x = 0.5(\text{M})$  phase is crystallographically and magnetically similar to the  $x = 0$  material and the same magnetic structures are observed as a function of temperature as shown by the evolution of magnetic peak intensities [31]. The onset of Mn spin order is between 100 and 200 K (estimated  $T_{\text{Mn}} \approx 130$  K), and the spin reorientation and  $\text{Re}^{5+}$  orbital ordering transition occurs at  $T_{\text{sr}} \approx 100$  K. It is notable that this is a higher temperature than in the undoped  $x = 0$  sample despite the introduced  $A$ -site cation disorder, and in keeping with the above suggestion that this is the same transition varying between 75 K in  $\text{Mn}_2\text{FeReO}_6$  and 140 K in  $\text{Ca}_2\text{FeReO}_6$ . Thermal variations of spin components and tilt angles in [31] show a similar switch in the Fe moment easy-axis at  $T_{\text{sr}} =$  as for undoped  $\text{Mn}_2\text{FeReO}_6$ .

The crystal and magnetic structures of the double double perovskite  $x = 0.5(\text{T})$  phase are found to be qualitatively the same as for the  $x = 1$  material, with high temperature ferrimagnetic order of the Fe and Re spins ( $T_{\text{C}} = 500$  K), and a second ferrimagnetic transition near  $T_{\text{Mn}} = 50$  K where Mn spins at the two distinct 4-coordinated sites in the  $A$ -site columns order antiparallel to each other as shown in Fig. 1. All ordered spins are parallel to the  $c$ -axis. No ordering of the Mn spins on Ca sites was observed.

Temperature variations of lattice parameters in Figs. 4c and d reveal magnetostructural anomalies at the  $T_{\text{sr}} = 100$  K spin reorientation transition for the  $x = 0.5(\text{M})$  phase, and at  $T_{\text{Mn}} = 50$  K for  $x = 0.5(\text{T})$ . The sharp increase in  $c$  below the 50 K Mn spin ordering for the  $x = 0.5(\text{T})$  double double perovskite phase leads to zero or negative thermal expansion between 25 and 50 K with calculated expansion coefficient  $\alpha_V = (1/V)(\Delta V/\Delta T) = -10(\pm 10) \times 10^{-6} \text{ K}^{-1}$ .

### **$\text{CaMnFeReO}_6$ ( $x = 1$ )**

As previously reported this sample adopts a single phase, double double perovskite structure in tetragonal  $P4_2/n$  space group with both  $A$  and  $B$ -site crystallographic order,  $A$ -site Ca/Mn order being of the columnar type and  $B$ -site Fe/Re order in a rock salt pattern [25]. Fe and Re spins order ferrimagnetically at  $T_{\text{C}} = 500$  K, and Mn spins order at a second ferrimagnetic transition at 70 K. The magnetic structure is collinear with all magnetic moments oriented along the  $c$ -axis, as shown in Fig. 1, and no magnetic reorientation transition was observed down to 2 K.

### **$\text{Ca}_{1.5}\text{Mn}_{0.5}\text{FeReO}_6$ ( $x = 1.5$ )**

Two phase behaviour is observed in PSXRD data with a majority (88.0(2) wt.%) monoclinic  $P2_1/n$  double perovskite  $x = 1.5(\text{M})$  phase and a minority double double perovskite  $x = 1.5(\text{T})$  phase with tetragonal  $P4_2/n$  symmetry present. The latter was fitted to PSXRD data using the model for  $x = 1$   $\text{CaMnFeReO}_6$  without varying site occupancies as attempts to refine the Ca/Mn ratio did not give statistically significant occupancy of Mn sites by Ca. Hence we estimate that the upper Ca limit for the  $x = 1.5(\text{T})$  double double perovskite phase is no more than  $x \sim 1.1$ . The contribution from the  $x = 1.5(\text{T})$  phase was too small to be refined in fits to the PND data, and only the majority  $x = 1.5(\text{M})$  crystal and

magnetic structures were fitted. Results are shown in Fig. 5 and in [31]. The composition of the  $x = 1.5(\text{M})$  phase is found to be  $(\text{Ca}_{1.73(8)}\text{Mn}_{0.27})\text{FeReO}_6$ , from site occupancy refinement during the PND fitting, so this likely represents the upper limit of Mn substitution for Ca in the  $\text{Ca}_2\text{FeReO}_6$  structure. The discovery that the  $x = 1.5(\text{T})$  and  $x = 1.5(\text{M})$  phases have respective refined  $x$  values of  $\sim 1.1$  and  $1.73(8)$  shows that a second miscibility gap exists in this Ca-rich region of the  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  system under the present synthesis conditions.  $5.3(2)\%$  Fe/Re- $B/B'$ -antisite disorder is found from the PSXRD fit for the  $x = 1.5(\text{M})$  phase, which is very similar to above values for  $x = 0.5(\text{M})$  and  $x = 0.5(\text{T})$  phases, demonstrating that the degree of  $B/B'$  site ordering is very constant across the series.

The magnetic behaviour of the  $x = 1.5(\text{M})$  phase shows qualitatively similar behaviour to that of the  $x = 2$   $\text{Ca}_2\text{FeReO}_6$  material [6,12], and no long range order of the A-site Mn spins is observed by PND, likely because of the low Mn concentration. The high temperature PND data are fitted by the same ferrimagnetic model as for  $\text{Mn}_2\text{FeReO}_6$ , with Fe/Re moments in the  $ac$ -plane, with only a small component along the  $a$ -axis and the majority of the spin directed along the  $c$ -axis. The Fe moments are near to the octahedral tilt direction,  $\theta_{\text{tilt}} \approx 20^\circ$ . Below  $T_{\text{sr}} = 100$  K there is a significant reorientation of Fe/Re spins and these gain significant  $y$ -components while remaining ferrimagnetically ordered. Anomalies in thermal expansion of Re-O bonds near the 100 K spin reorientation (Fig. 5d) are consistent with a  $\text{Re}^{5+}$  orbital ordering transition, suppressed from the 140 K value reported for  $\text{Ca}_2\text{FeReO}_6$  [12] by Mn-doping. Electronic phase separation was previously reported in some studies of  $\text{Ca}_2\text{FeReO}_6$  [13,14] and may result from different spin-orbit coupled phases but we do not observe any such separation in the  $x = 1.5(\text{M})$  double perovskite phase  $(\text{Ca}_{1.73}\text{Mn}_{0.27})\text{FeReO}_6$  here.

## 2 X-ray Magnetic Circular Dichroism

As neutron diffraction intensities are insensitive to  $S = 1$   $\text{Re}^{5+}$  moments in the presence of large ordered  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$   $S = 5/2$  spins, the Re magnetism has been further investigated using X-ray Magnetic Circular Dichroism (XMCD). X-ray Absorption Near-Edge Spectra (XANES) and the derived XMCD data for Re  $L_2$  and  $L_3$ -edges are shown for the  $x = 0$  sample ( $\text{Mn}_2\text{FeReO}_6$ ) in Fig. 6, and similar spectra for  $x = 1$  and  $1.5$  are shown in [31]. Qualitatively, XANES and XMCD spectral shapes bear strong similarities with those in former studies of  $A_2\text{FeReO}_6$  double perovskites with  $A = \text{Ca}, \text{Sr},$  or  $\text{Ba}$  [33,34,35,36]. Re XANES spectra for all  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  samples have same shapes and edge positions (within  $\sim 0.2$  eV) indicating that Re valence remains essentially constant with Mn for Ca substitution. A double-peak white-line structure is observed at both Re  $L_2$  and  $L_3$ -edges. The white line peak splitting of  $\sim 3.0$  eV reflects the octahedral crystal-field splitting of the  $5d$  orbitals of  $\text{Re}^{5+}$  into  $t_{2g}$  and  $e_g$  states [33,35,36,37]. While XMCD at the Re  $L_3$  edge shows a differential shape of limited integral, a largely dominant negative XMCD signal is observed at the  $L_2$  edge which indicates Re spin moments aligned antiparallel to the applied field. More quantitatively, spin ( $m_S$ ), orbit ( $m_L$ ) and total ( $m = m_S + m_L$ ) moments for Re moments were derived by applying standard sum rules [38,39] to the



integrals of the XANES and XMCD spectra in the vicinity of the absorption edge. The magnetic dipole operator  $\langle T_Z \rangle$  is neglected as done in previous reports on closely related double perovskites [33,34,35,37]. The number of  $d$ -state electron holes is taken to be  $n_h = 8$  (corresponding to the closest integral charge distribution,  $\text{Ca}_x\text{Mn}_{2-x}\text{Fe}^{3+}\text{Re}^{5+}\text{O}_6$ ) although values calculated for  $n_h = 9$  ( $\text{Ca}_x\text{Mn}_{2-x}\text{Fe}^{2+}\text{Re}^{6+}\text{O}_6$ ) differ by  $<0.1 \mu_B$ . Results are summarised in Table II, and the field dependence of the Re  $L_2$  XMCD signal for  $\text{Mn}_2\text{FeReO}_6$  is shown in Fig. 6d.

The Re XMCD results demonstrate that Re moments in  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  spin ordered structures are negative (antiparallel to the majority Fe moments), in keeping with the expected ferrimagnetism. A substantial orbital moment is present as expected for orbitally-degenerate  $5d^2 \text{Re}^{5+}$  and does not show any dependence on  $x$ , but does increase slightly at low temperatures. At 290 K, the orbital-to-spin moment ratio  $|m_L/m_S|$  –which is independent of the estimate of  $n_h$ – amounts to 0.28, 0.29 and 0.33 for  $x = 0, 1$  and  $1.5$ , respectively. These ratios are close to those reported (0.27-0.34) for  $\text{A}_2\text{FeReO}_6$  double perovskites with non-magnetic atoms on the  $A$  site [33,34,35]. For  $\text{Mn}_2\text{FeReO}_6$ , the temperature evolution of the  $|m_L/m_S|$  ratio appears to be non-negligible (increasing to 0.39 at 2.2 K) and the total moments at 2.2 and 100 K are smaller than those at 290 K (Table II). This is likely to be a result of canting in the Fe/Re spin structure, as XMCD only reflects a net magnetic moment along the applied magnetic field direction. This provides further evidence for a canting of the Fe/Re sublattice due to Mn spin order and  $\text{Re}^{5+}$  orbital order. We also note that while the XMCD field dependence for Re shows a rapid moment alignment at low field (below 0.5 T), it is not fully saturated even in a 17 T field, so that the intrinsic moment of Re may be underestimated. Fields in excess of 30 T are reported to be needed to fully saturate  $\text{Ca}_2\text{FeReO}_6$  [6,40].

Mn K-edge XMCD data were also collected for  $\text{Mn}_2\text{FeReO}_6$  (Fig. 6c). The field-dependence of the XMCD signal (Fig. 6e) shows a rapid alignment of the Mn moments and reveals a small magnetic hysteresis. The shape and magnitude of the high field Mn XMCD spectra do not differ greatly between 295 K (where Mn spins are paramagnetic), 100 K (induced Mn order) and 2.2 K (Mn spins reoriented). This suggests that the orbital moment on the Mn  $4p$  states is strongly influenced by neighbouring Fe/Re atoms and only is weakly affected by the development of the antiferromagnetic order of Mn at low temperature.

### 3 Magnetisation

Magnetization plots in Fig. 7a show that all of the  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  samples display ferrimagnetism with high ordering temperatures of  $T_C = 500$  to  $550$  K. However, it is not possible to distinguish  $T_C$  values for the double and double double perovskite phases within the two-phase  $x = 0.5$  and  $x = 1.5$  samples, and their Curie transitions are not broader than those of the single phase  $x = 0$  and  $1.0$  samples. Hence it is likely that the double and double double perovskite phases have very close  $T_C$

's showing that the strength of the Fe-Re magnetic exchange varies little with structure type or composition in this system. Features due to *A*-site Mn ordering and  $\text{Re}^{5+}$  orbital ordering transitions are also evident. In the Mn-rich double perovskites, the spin reorientation transition is evident by a maximum at 75 K for  $x = 0$ , and an inflection at 100 K for the  $x = 0.5(\text{M})$  phase. Mn-spin order in the  $x = 0.5(\text{T})$  and  $x = 1$  double double perovskites gives rise to a low temperature upturn in magnetisation. This corresponds to the second ferrimagnetic transition of Mn spins in the two different *A*-column sites, as evidenced by the data in Fig 7b.

Low- $x$   $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  samples have small magnetic coercivities of  $<0.1$  T at low temperatures. However, coercive field increases to 0.5 T for the  $x = 1.5(\text{M})$  sample, in keeping with the 0.95 T value reported for  $x = 2$  [12]. Although the  $\text{Re}^{5+}$  orbital ordering transition is observed across the range of double perovskite phases, it appears that the replacement of non-magnetic Ca by magnetic Mn lowers the anisotropy of the system.

## Discussion and Conclusions

A phase diagram for the  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  system and variations of magnetic and lattice parameters with  $x$  derived from the above results are shown in Fig. 8. These show the determined compositions for the  $x = 0.5(\text{M})$  and  $x = 0.5(\text{T})$  and the  $x = 1.5(\text{M})$  and  $x = 1.5(\text{T})$  materials in the phase-separated samples. Although  $\text{Ca}_2\text{FeReO}_6$  and  $\text{Mn}_2\text{FeReO}_6$  are both monoclinic  $P2_1/n$  double perovskites with quite similar lattice parameters, their  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  solid solution range is limited to the  $0 < x < 0.17$  and  $1.73 < x < 2$  end regions. This demonstrates similar small levels of substitution in the two members under the 10 GPa and 1673 K synthesis conditions used here, i.e. up to 8.5% Ca substitutes in  $\text{Mn}_2\text{FeReO}_6$  and up to 13.5% Mn in  $\text{Ca}_2\text{FeReO}_6$ . The central region of the phase diagram is occupied by the tetragonal  $P4_2/n$  double double perovskite of ideal composition  $\text{CaMnFeReO}_6$  where Ca and Mn cations are ordered into distinct *A*-site columns. This phase is found to have composition range  $0.74 < x < \sim 1.1$ , showing that up to 26% Mn can be substituted at the 10-coordinate Ca sites in the double double perovskite structure, but only a small amount  $\sim 10\%$  of Ca can replace Mn. This likely reflects the small size of the 4-coordinated  $\text{Mn}^{2+}$  *A*-sites. The limited substitutions of Ca and Mn for each other in both the double and double double perovskite structures result in substantial co-existence regions. Analysis of the nominal  $x = 0.5$  and 1.5 samples reveals that the two-phase regions cover  $0.17 < x < 0.74$  and  $\sim 1.1 < x < 1.73$  compositions. No other phases are found in the  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  system.

The large co-existence regions of double and double double perovskite structures appear surprising in view of previous work on the  $\text{RMnMnSbO}_6$  ( $R$  = rare earth) series, the only other system reported so far in which both structure types appear [26].  $R$  = La, Pr, Nd, Sm materials formed tetragonal

$P4_2/n$   $RMnMnSbO_6$  double double perovskites with full  $A/A'$ -ordering of  $R^{3+}$  and  $Mn^{2+}$  cations, whereas monoclinic  $P2_1/n$   $(R_{0.5}Mn_{0.5})_2FeReO_6$  double perovskites with no long range  $R^{3+}/Mn^{2+}$  order were found for  $R = Eu$  and  $Gd$ . No secondary phase of a double perovskite was observed for  $R = Sm$  and no double double impurity was seen for  $R = Eu$  despite the very similar ionic radii of their  $R^{3+}$  cations, demonstrating that the structural boundary is sharp with no apparent co-existence region. The key distinction may be the charge difference between  $R^{3+}$  and  $Mn^{2+}$  cations which disfavors separation into two  $R_yMn_{2-y}MnSbO_6$  phases with  $y \neq 1$  as there is no facile charge compensation mechanism, whereas segregation of  $Ca^{2+}$  and  $Mn^{2+}$  in the  $Ca_xMn_{2-x}FeReO_6$  system can occur without need for charge compensation. There are clearly many opportunities to explore double - double double perovskite relationships in other  $(A,A')_2BB'O_6$  systems using high pressure.

All  $Ca_xMn_{2-x}FeReO_6$  compositions are found to be ferrimagnetic with Curie temperatures near 500 K. This demonstrates that the  $B$ -site  $Fe/Re$  spin order is robust with exchange interactions that are relatively insensitive to the structure type and cation ordering between double and double double perovskite types. XMCD confirms that  $Re$  moments are antiparallel to the bulk magnetisation direction determined by the  $Fe$  and  $Mn$  spins, and show large orbital moments consistent with the orbital ordering at low temperatures. It was not possible to distinguish separate  $T_C$  's for the double and double double perovskite phases within the mixed phase  $x = 0.5$  and  $1.5$  samples. The highest values of  $T_C = 520$  and  $540$  K are found for  $Mn_2FeReO_6$  and  $Ca_2FeReO_6$  respectively, with disorder due to substitution by  $Ca$  or  $Mn$  lowering the transition temperature. Low temperature  $Mn$  spin order is observed in the  $Mn$ -rich double perovskites and the double double perovskite phases, with the maximum ordering temperature of  $175$  K at the highest  $Mn$ -content ( $x = 0$ ). However,  $Mn$  spins within the  $Ca$ -rich  $1.73 \leq x < 2$  double perovskite region remain paramagnetic to the lowest measured temperatures. Spin reorientation transitions accompanying orbital ordering of  $5d^2 Re^{5+}$  are observed across all of the double perovskites, with  $T_{sr}$  falling from  $140$  K in  $Ca_2FeReO_6$  to  $75$  K in  $Mn_2FeReO_6$ . However, no spin reorientation or Jahn-Teller distortion of  $ReO_6$  octahedra is evident for the double double perovskite phases, and this may be suppressed by the rigidity of the  $B/B'O_6$  network and large octahedral tilt angles within this structural type.

The maximum low-temperature magnetisation, measured at  $7$  T, decreases slightly with rising  $x$ , from  $4.6 \mu_B$  at  $x = 0$  to  $4.0 \mu_B$  at  $x = 1.5$ , and then falls to  $2.4 \mu_B$  in  $Ca_2FeReO_6$  (Fig. 7b). Estimated values from the ordered moments observed by neutron scattering are lower for  $x = 0$  to  $1.5$  samples, but similar to the maximum magnetisation at  $x = 2$ . These observations demonstrate that the paramagnetic (in  $Mn$ -rich double perovskites) or ferrimagnetic (in the double double phases)  $A$ -site  $Mn$  spins supplement the magnetisation due to ferrimagnetic order of  $B$ -site  $Fe^{3+}$  and  $Re^{5+}$  moments.  $Mn$ -rich materials are soft magnets with coercive fields  $< 0.1$  T at low temperatures, but the  $Ca$ -rich double perovskites have significant magnetic anisotropy with a coercive field of  $0.95$  T reported for

$\text{Ca}_2\text{FeReO}_6$ . The variations in coercivity do not reflect changes in structural anisotropy, as the monoclinic lattice distortion and low temperature orbital order are fairly constant across all the double perovskite compositions, and so probably reflect the presence of *A*-site Mn spins that lower the energy barrier to Fe/Re spin reversal at low  $x$ .

In summary, only a limited range of  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  solid solutions close to the end members ( $0 < x < 0.17$  and  $1.73 < x < 2$ ) are formed between  $\text{Mn}_2\text{FeReO}_6$  and  $\text{Ca}_2\text{FeReO}_6$ , despite both having monoclinic  $P2_1/n$  double perovskite structures with similar lattice parameters. Additional 1:1 *A*-site ordering stabilises a double double perovskite phase based on the structure of  $\text{CaMnFeReO}_6$  for  $0.74 < x < \sim 1.1$ . Wide regions of double – double double perovskite phase coexistence occur between these limits. This is likely due to the facile segregation of  $\text{Ca}^{2+}$  and  $\text{Mn}^{2+}$  cations between the two structure types, unlike in the previously reported  $\text{RMnMnSbO}_6$  system where no phase separation was observed. All  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  compositions are found to be ferrimagnetic with Curie temperatures for Fe/Re spin order near 500 K. Mn spin order is observed below 175 K in the Mn-rich double perovskites and the double double perovskite phases, but Mn spins within Ca-rich  $1.73 \leq x < 2$  double perovskites remain paramagnetic to below 2 K. A spin reorientation transition accompanying orbital ordering of  $5d^2 \text{Re}^{5+}$  is observed across the double perovskites, decreasing from 140 K at  $x = 2$  to 75 K at  $x = 0$ . XMCD confirms that Re moments are antiparallel to Fe and Mn spins, and show large orbital moments consistent with the orbital ordering. However, no orbital ordering transition is observed in the double double perovskite phases, likely due to the rigidity and large octahedral tilt angles of this structural type. High pressures are required to access these materials, and future investigation of other transition metal  $(A,A')_2BB'\text{O}_6$  systems may lead to discoveries of other interesting electronic and magnetic materials.

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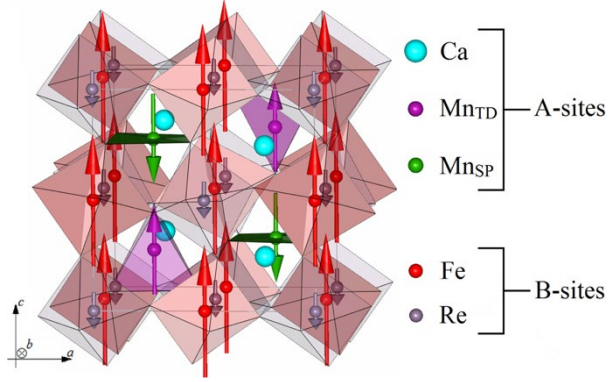
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**Table I** Room temperature lattice parameters and magnetic ordering transition temperatures ( $T_C$  – Curie,  $T_{Mn}$  – A-site Mn spin order, and  $T_{sr}$  – spin reorientation and Re-orbital order) for  $Ca_xMn_{2-x}FeReO_6$  samples. Double and double double perovskite phases respectively have monoclinic space group (S. G.)  $P2_1/n$  and tetragonal  $P4_2/n$ . Curie temperatures are determined from magnetization data, with only a single value measured for the two-phase  $x = 0.5$  and 1.5 samples. All other values are from PND, except for the  $x = 1.5$   $P4_2/n$  phase which was only analyzed from PSXRD data,

| Nominal $x$              | 0            | 0.5          |          | 1         | 1.5          |           | 2          |
|--------------------------|--------------|--------------|----------|-----------|--------------|-----------|------------|
| S.G.                     | $P2_1/n$     | $P2_1/n$     | $P4_2/n$ | $P4_2/n$  | $P4_2/n$     | $P2_1/n$  | $P2_1/n$   |
| Refined $x$              | 0            | 0.17(3)      | 0.74(2)  | 1         | 1            | 1.73(8)   | 2          |
| $a / \text{\AA}$         | 5.2087(4)    | 5.2339(7)    | 7.612(1) | 7.6311(5) | 7.66839(6)   | 5.3843(7) | 5.39023(6) |
| $b / \text{\AA}$         | 5.3687(5)    | 5.3929(7)    | -        | -         | -            | 5.5168(7) | 5.51648(6) |
| $c / \text{\AA}$         | 7.5998(6)    | 7.610(1)     | 7.603(1) | 7.6266(7) | 7.64776(7)   | 7.683(1)  | 7.67191(8) |
| $\beta / \text{degrees}$ | 90.06(2)     | 89.95(2)     | -        | -         | -            | 89.996(5) | 90.2212(6) |
| $T_C / \text{K}$         | 520          | 500          |          | 500       | 490          |           | 540        |
| $T_{Mn} / \text{K}$      | 175          | 130          | 75       | 70        | -            | -         | -          |
| $T_{sr} / \text{K}$      | 75           | 100          | -        | -         | -            | 100       | 140        |
| Reference                | [This study] | [This study] |          | [25]      | [This study] |           | [12]       |

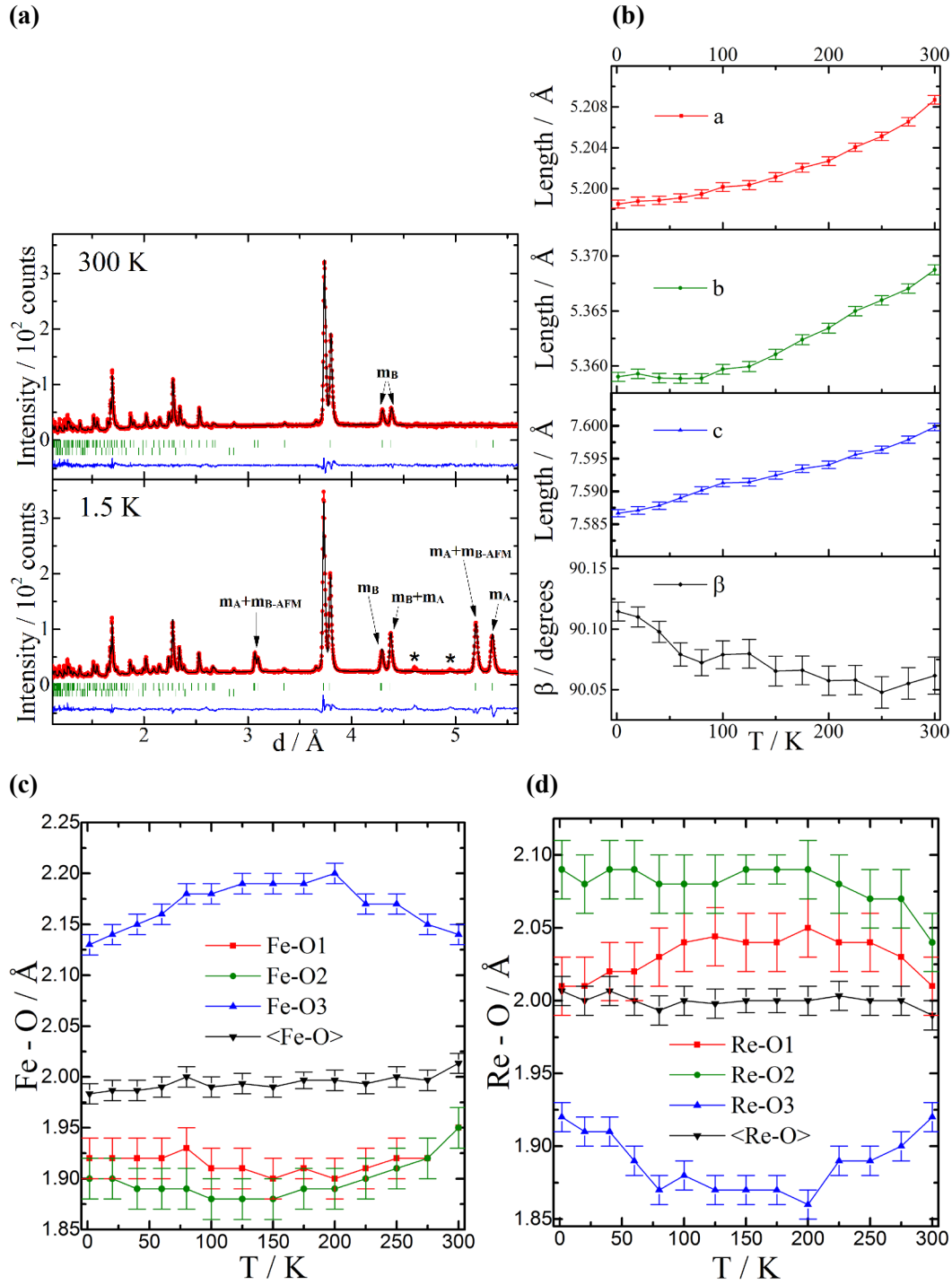
**Table II** Calculated spin ( $m_S$ ), orbit ( $m_L$ ) and total ( $m = m_L + m_S$ ) moments for Re derived from XMCD data for  $Ca_xMn_{2-x}FeReO_6$  samples recorded in a 2 T magnetic field at several temperatures and considering a magnetic dipole operator  $\langle T_Z = 0 \rangle$ .

| $x$ | $T$ (K) | $m_S$ ( $\mu_B$ ) | $m_L$ ( $\mu_B$ ) | $m$ ( $\mu_B$ ) |
|-----|---------|-------------------|-------------------|-----------------|
| 0   | 290     | -0.74             | 0.21              | -0.53           |
| 0   | 100     | -0.64             | 0.24              | -0.40           |
| 0   | 2.2     | -0.72             | 0.28              | -0.44           |
| 1.0 | 290     | -0.48             | 0.14              | -0.34           |
| 1.0 | 2.2     | -0.72             | 0.21              | -0.51           |
| 1.5 | 290     | -0.66             | 0.22              | -0.45           |

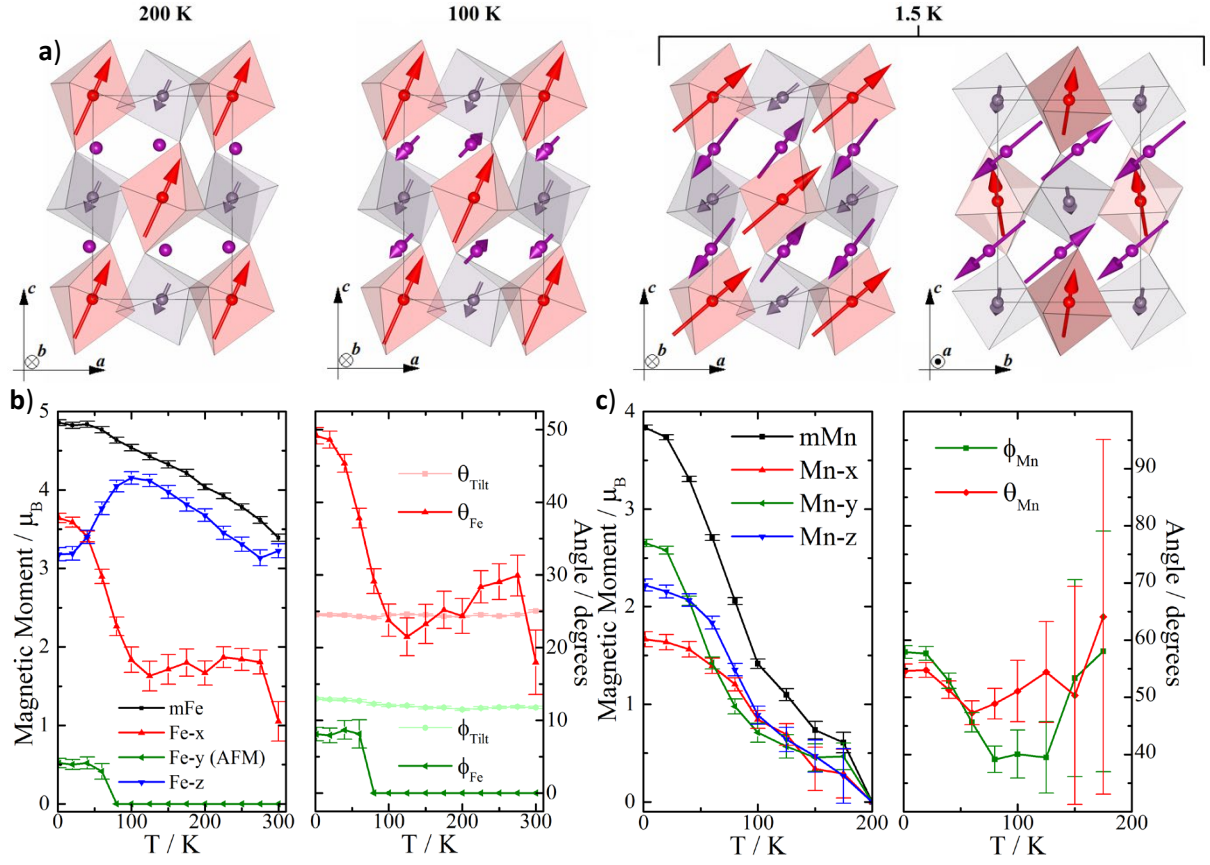


**FIG. 1** Crystal and magnetic structures of the tetragonal  $P4_2/n$   $AA'BB'O_6$  double double perovskite  $\text{CaMnFeReO}_6$  showing columnar  $A/A'$ -Ca/Mn and rocksalt  $B/B'$ -Fe/Re cation orders. The  $\text{Mn}^{2+}$  cations occupy alternating tetrahedral ( $\text{Mn}_{\text{TD}}$ ) and square planar ( $\text{Mn}_{\text{SP}}$ ) sites within their column. There are thus five different cation sites in total in this structure type. Ferrimagnetic orders of Fe/Re and of  $\text{Mn}_{\text{TD}}/\text{Mn}_{\text{SP}}$  spins are observed at low temperatures.

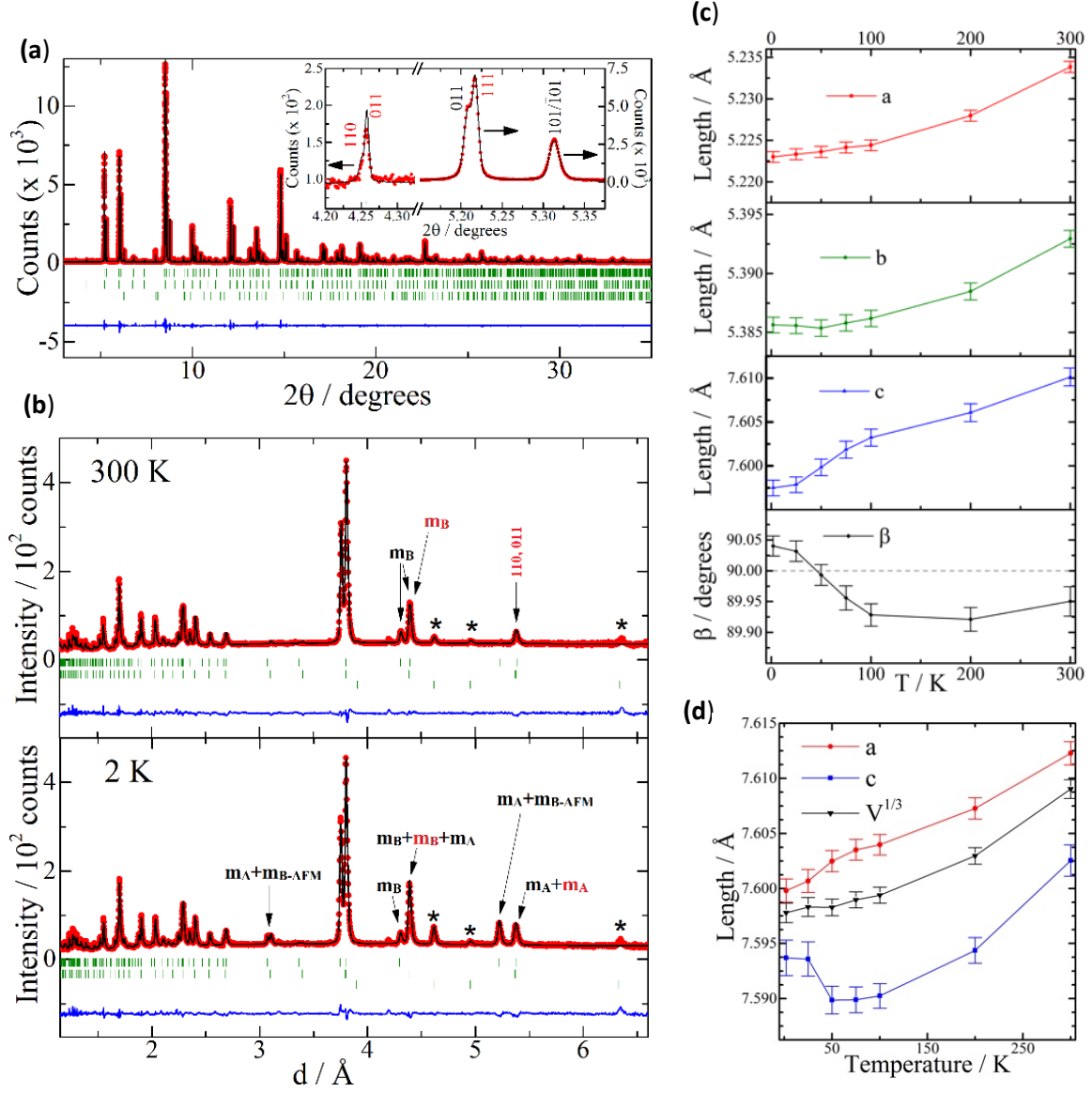




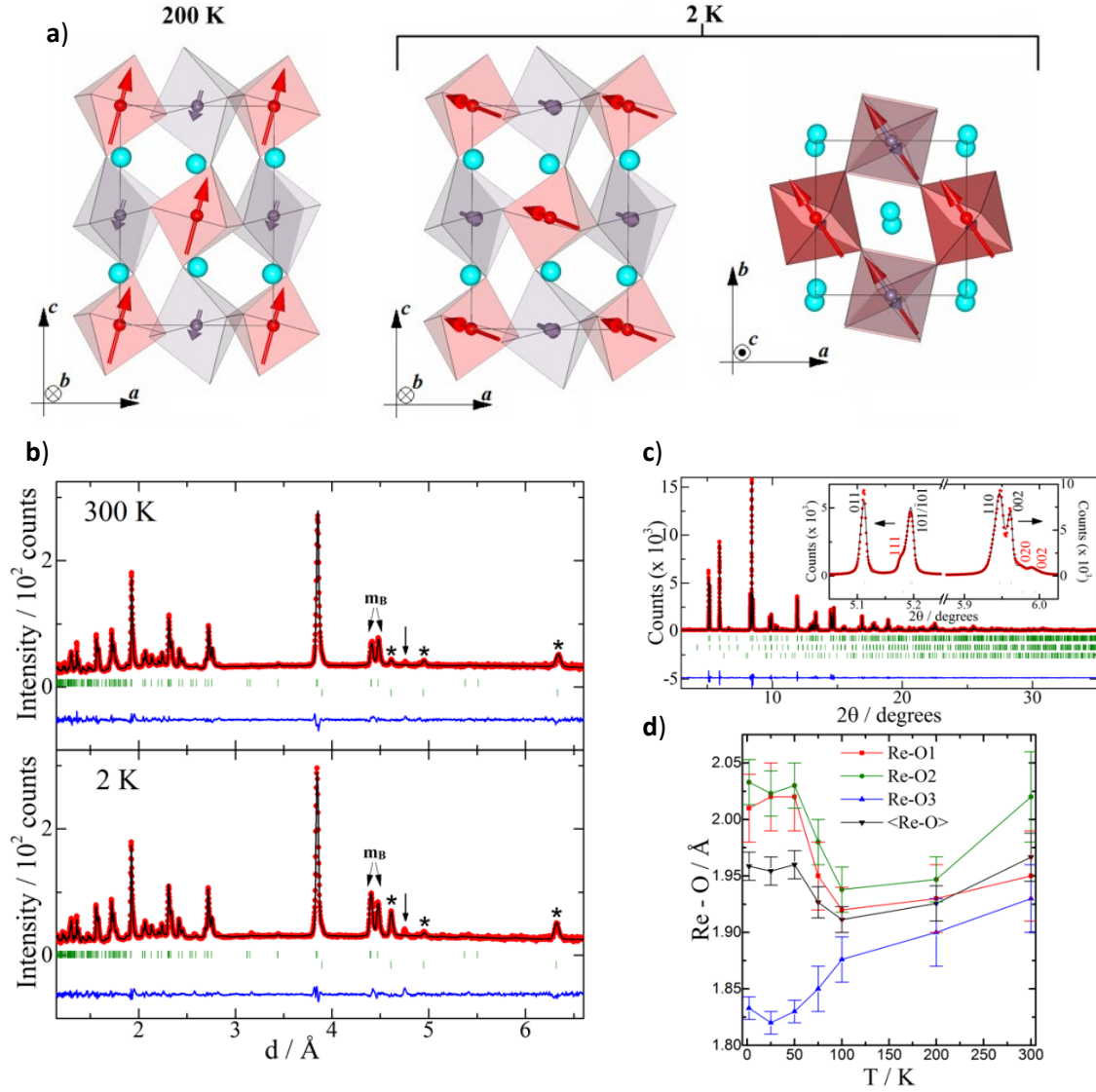
**FIG. 2** Powder neutron diffraction results for  $\text{Mn}_2\text{FeReO}_6$ . (a) Profile fits at 1.5 and 300 K. Labels  $m_A$  and  $m_B$  refer to magnetic reflections with contributions from  $A$  (Mn) and  $B$  (Fe/Re) site spin order, respectively. Lower markers show the fit of a trace of  $\text{ReO}_2$  impurity, and asterisks mark peaks from a trace of  $\text{MnFe}_3\text{O}_5$ . Plots show temperature variations of refined quantities for  $\text{Mn}_2\text{FeReO}_6$ ; (b) monoclinic lattice parameters, (c) Fe-O bond lengths, and (d) Re-O bond lengths.



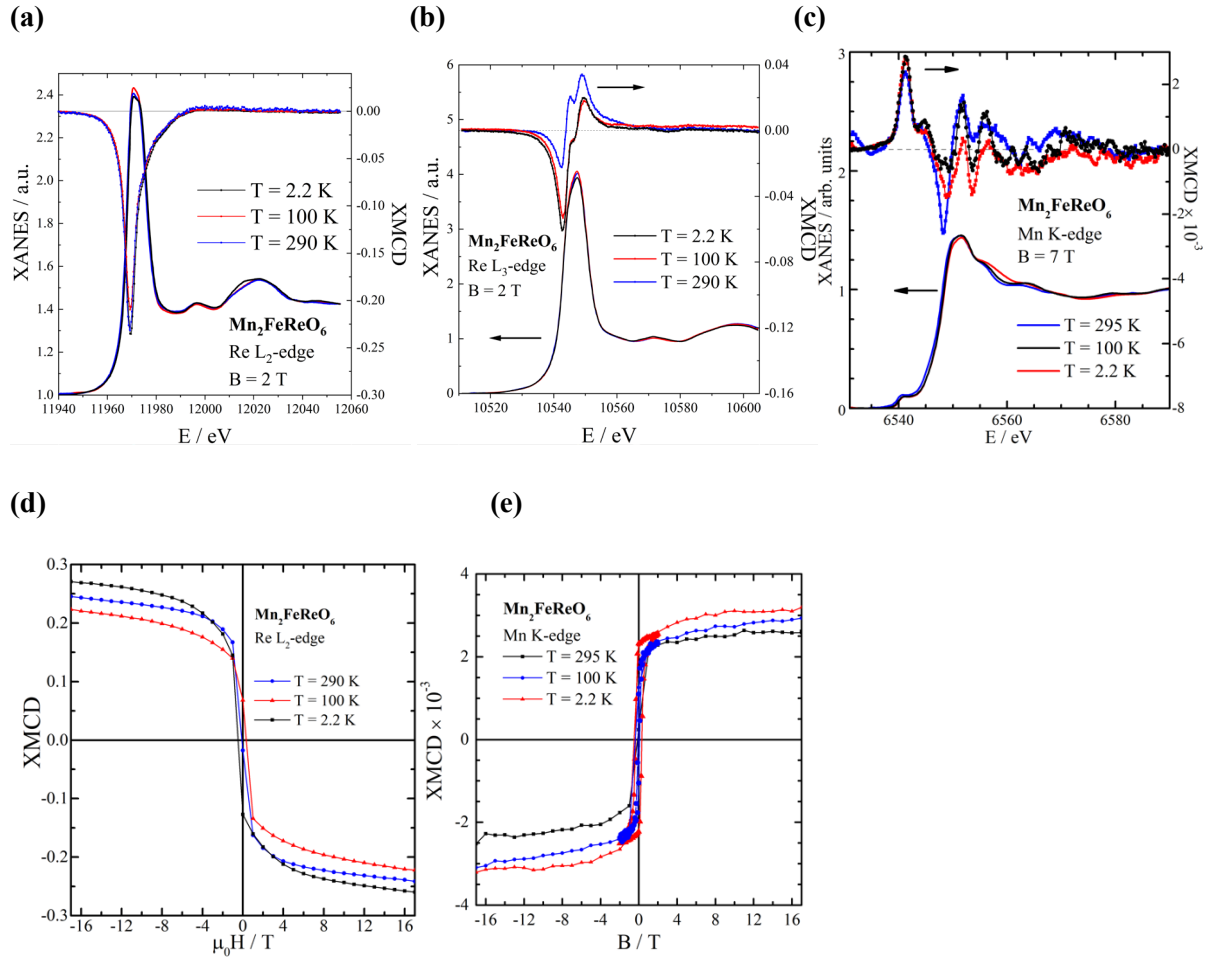
**FIG. 3.** (a) Refined magnetic structures of  $\text{Mn}_2\text{FeReO}_6$  at 200, 100 and 1.5 K. Fe atoms are shown in red, Re in grey and Mn in purple. The 1.5 K magnetic structure is shown in the  $ac$ -plane, as well as the  $bc$ -plane to emphasise the  $b$ -axis antiferromagnetic Fe/Re component to the spin order. Plots show (left) the total magnetic moment and cartesian components of spin order, and (right) tilt angles for (b) Fe and (c) Mn spins.  $\theta_{\text{Fe(Mn)}}$  is the angle between the  $c$ -axis and the Fe(Mn) spin direction in the  $ac$ -plane.  $\phi_{\text{Fe(Mn)}}$  is the angle between the  $a$ -axis and the Fe(Mn) spin direction in the  $ab$ -plane. Angles  $\theta_{\text{Tilt}}$  and  $\phi_{\text{Tilt}}$  in (b) show the tilts of the  $\text{FeO}_6$  octahedra defined correspondingly.



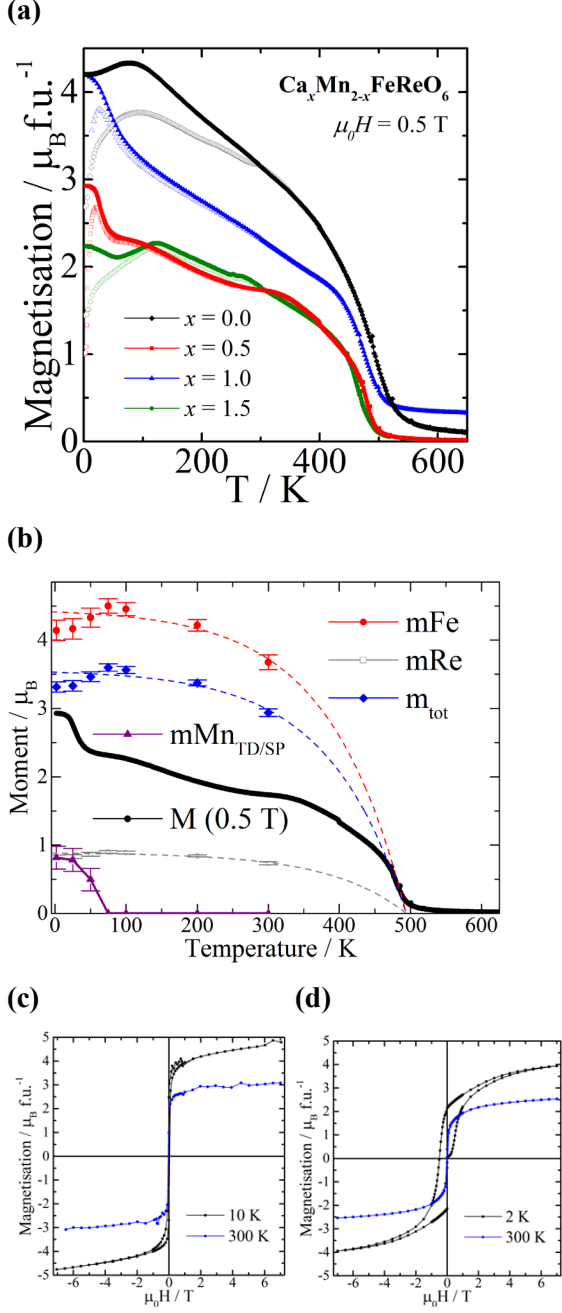
**FIG. 4.** Results for the nominal  $\text{Ca}_{0.5}\text{Mn}_{1.5}\text{FeReO}_6$  ( $x = 0.5$ ) sample. Fits to (a) 300 K PSXRD and (b) 2 and 300 K PND profiles. The  $x = 0.5(\text{T})$  phase is indicated with red labels, while the  $x = 0.5(\text{M})$  phase is indicated by black labels. Designations  $m_A/m_B$  indicate reflections that have magnetic contributions from  $A$  or  $B$ -site spin order and  $m_{B\text{-AFM}}$  refers to the antiferromagnetic component of Fe/Re spin order along the  $b$ -axis due to frustration. Asterisks mark a small  $\text{MnFe}_3\text{O}_5$  impurity. Thermal variations of PND lattice parameters for (c)  $x = 0.5(\text{M})$  and (d)  $x = 0.5(\text{T})$  phases.



**FIG. 5.** Results for the nominal  $\text{Ca}_{1.5}\text{Mn}_{0.5}\text{FeReO}_6$  ( $x = 1.5$ ) sample. (a) Crystal and magnetic structures of the  $x = 1.5$ (M) phase at 200 and 2 K. Fe atoms are shown in red, Re in grey and Ca/Mn sites in cyan. Magnetic spin structures are shown in the  $ac$ -plane as well as the  $ab$ -plane at 2 K regime to show spin orientation. (b) 2 and 300 K PND patterns showing the fit of the  $x = 1.5$ (M) phase. Reflections marked as  $m_B$  have magnetic contributions from B-site magnetic order, no ordered moment from A-site Mn is observed from PND. Asterisks mark a small  $\text{MnFe}_3\text{O}_5$  impurity. (c) PSXRD data at 300 K. Rows of markers from top to bottom indicate the  $x = 1.5$ (M) double perovskite phase (88.0(2)% by weight,  $hkl$  indices in the inset in black), the  $x = 1.5$ (T) double double perovskite phase (11.88(6) % by weight, indices in red), and  $\text{ReO}_2$  impurity (0.09(1) % by weight). (d) Thermal variations of PND Re-O bond distances in the  $x = 1.5$ (M) structure.



**FIG. 6.** X-ray Absorption Near-Edge Spectra (XANES) and X-ray Magnetic Circular Dichroism (XMCD) data for  $\text{Mn}_2\text{FeReO}_6$  at (a) Re  $L_2$ -edge, (b) Re  $L_3$ -edge and (c) Mn K-edge, at several temperatures. XMCD hysteresis of (d) the Re  $L_2$ -edge and (e) the Mn K-edge signals.



**FIG. 7.** Magnetization measurements for  $\text{Ca}_x\text{Mn}_{2-x}\text{FeReO}_6$  samples. (a) Field cooled (filled symbols) and zero field cooled (open symbols) for all samples in a 0.5 T field. (b) Field cooled magnetization for the  $x = 0.5$  sample, compared against moments at the Mn, Fe, and Re sites and the net moment  $m = m_{\text{Fe}} - m_{\text{Re}}$  from neutron refinements of the  $x = 0.5(\text{T})$  double double perovskite phase. Magnetic hysteresis data for (c) the  $x = 0.5$  and (d) the  $x = 1.5$  samples.

